SURFACTANT ASSISTED PHASE TRANSFER OF WATER-INSOLUBLE QUANTUM DOTS

BY

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THESIS

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ABSTRACT

Nanotechnology is believed to have the potential of solving the biggest challenges for human beings in areas such as environment protection, renewable energy, and disease detection and treatment. At the same time, this new technology could also pose unknown potential risk to the environment. While commercialization of nanotechnology is growing rapidly across a wide range of products, regulation of nanotechnology to limit the negative impacts is currently lacking.

Among the impacts of nanotechnology on the environment, we are specifically interested in the transformation of nanomaterials in the aqueous environment and their subsequent fate. The primary objective of the research presented in this thesis is to study the role of surfactants in facilitating the phase transfer of hydrophobic nanomaterials from organic solvents into the aqueous phase. Without surfactants, hydrophobic nanomaterials would aggregate into micro-scale aggregates in water, potentially reducing their bio-availability, mobility, and toxicity. However, biologically produced surfactant-like molecules are ubiquitous in the aqueous environment, and it might alter the hydrophobic surface into hydrophilic, increasing the environmental risk. Hence, the risk of hydrophobic nanomaterials in the environment may be underestimated.

To investigate the potential phase transfer phenomenon, we have chosen a model experimental system consisting of quantum dots (QDs), a nanoparticle with fluorescence and a model surfactant, to study their interaction. A new scenario of quantum dots phase transfer in aqueous environment was proposed. The experimental result shows that there are several factors that affect the extent of phase transfer. These include the rate of addition of organic QDs solution to the surfactant solution and absolute and relative concentrations of surfactant and QDs. The lower the ratio, the higher phase transfer efficiency. Also, as the concentration of surfactant increases, the phase transfer efficiency will increase, as well as the saturation concentration of the phase transferred quantum dots. The stability of the phase transferred quantum dots is determined by the strength of the surfactant. With the surfactant we have tested, the phase transferred QDs eventually forms aggregates and settles out.

After investigating the phase transfer of QDs, we are currently investigating the toxicity of these phase transferred QDs on *Synechococcus elongatus* as well as on microbial communities in an anaerobic bio-digester.

Contents

Chapter 1

Introduction

1.1 Concerns about nanotechnology and nanomaterials

1.1.1 Nanotechnology and nanomaterials

Nanotechnology is the ability to create functional materials with nanometer scale features. This includes understanding the properties of materials with nano-scale structures as well as the the technology to create and use them[1]. Figure 1.1 shows ontology of nanotechnology[21]. We can see that nanotechnology encompasses a wide variety of materials, methods and applications.

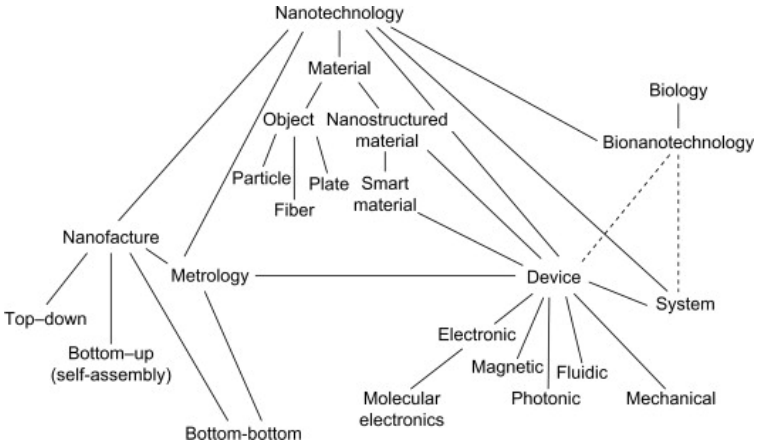


Figure 1.1: Classification of nanotechnologies

Among its ontology, nanomaterials(NMs) are materials and objects with at least one dimension under 100 nm, within which nanoparticles (NPs) are confined to sizes between 1 to 100 nm in three

dimensions[2].

While the NMs defined in nanotechnology are the engineered nanomaterials, under a broader definition, NMs are categorized into three groups, natural, incidental and engineered. Natural NMs are created by natural processes, such as inorganic NMs produced from volcanic eruptions, forest fires and hydrothermal vent systems and organic NMs like pollen fragments and virus [17, 16]. Within this group, NPs in air are denoted as ultra-fine particles, and colloids in water and soil [13]. They are an ecologically essential component. Instances of their existences are aquatic sediments, microbial products, "nanofossils" [9].

Incidental NMs are produced by human activity accidentally, such as combustion. Fossil fuel combustion can introduce a significant amount of NPs into the environment, resulting in deleterious environmental and health effects[17, 9, 3].

1.1.2 Engineered nanomaterials

Engineered nanomaterials (ENMs) are produced by nanotechnology for a defined purpose. They possess special properties because of their highly ordered structure and homogeneity [17]. The advantages of nanotechnology that have led to its appeal include a new way to create combinations of features (composite nano-structures, NMs integrated bulk materials) and resource and energy use reduction due to enhanced functionality[21]. Motivated by these advantages, a variety of products that incorporate nanotechnology have been developed. Nanomaterials can be classified into two categories, discrete nano-scale materials and nano-structured materials. Discrete nanoscale is categorized into three groups according to the number of external dimensions in nanoscale, as shown in figure 1.2 [22], while a nano-structured material is a material possessing internal or surface structure under 100 nm [22].

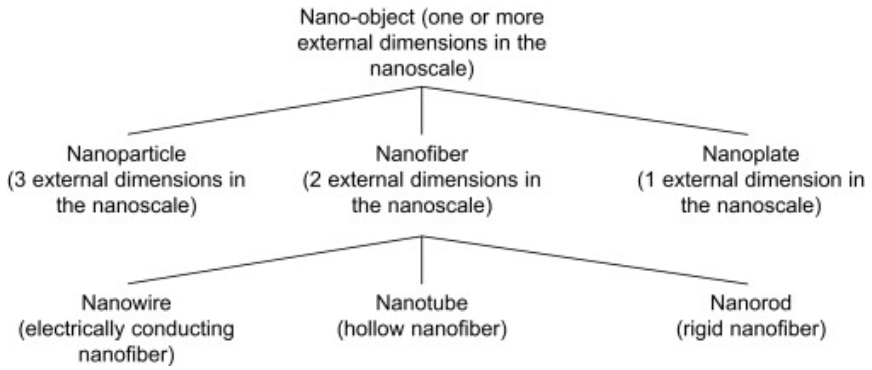
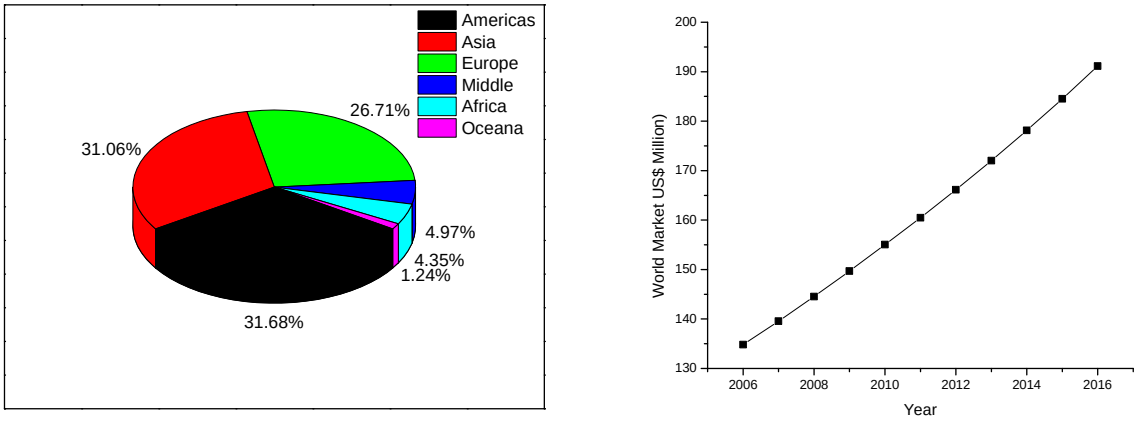


Figure 1.2: Classification of nano-scale materials

The recent and projected use of nanoparticle in composites is shown in figure 1.3a and figure 1.3b [18]. The data shows that, the Americas, Asia and Europe are the main areas consuming nano-products. The market is also projected to grow steadily in the near future.



(a) World market for nanoparticles in composites, US$ Million, 2011

(b) World market for nanoparticles in composites: 2006 - 2016

Figure 1.3: World market for nanoparticles

Many exciting technological advances are expected from the applications of nanomaterials. Nanotechnology is expected to improve therapies for challenging diseases[20], advance environmental technology such as nanoparticle integrated membranes for clean water[28], reduce poverty by proving more economic and better performance utilities to the poor[4], and help food section through new solutions like nanoencapsulation of nutraceuticals[26], which are all the most serious problems challenging our society nowadays. However, the environmental impact of nanotechnology has to be minimized to avoid the potential hazard.

1.1.3 Quantum dots (QDs)

When a particle is confined at nano-scale in all three dimensions, it is called "quantum dot". It is small but not too small to have a well-defined lattice. To explain the energy levels in a quantum dot, we need to classify materials into three categories: metal, semiconductor, and insulator. For metal nanoparticles, when photons resonate with the electrons on their surface, surface plasmons happen, which is strongly related to the size of the nanoparticles.

When the dimensions of a semi-conducting material are shrunk to a size comparable to Exciton Bohr radius, the nanoparticle works like a confinement box for the electron-hole pair generated by an incident photon. It squeezes the radius of the electron orbit around the hole, increasing the confinement energy. And the energy gap (E_{g}) of QDs is:

$$E_{\mathrm{g}}(dot) = E_{\mathrm{g}}(bulk) + E_{\mathrm{well}} + E_{\mathrm{Coul}}$$

$E_{\mathrm{well}}$is the confinement energy and E_{Coul} is Coulomb energy. E_{well} (positive) is always larger than E_{Coul} (negative). So $E_{\mathrm{g}}(dot)$ always has a higher value than E_{bulk} [24]. Only photons with energy higher than $E_{\mathrm{g}}(dot)$ can excite the electron and cause an electron-hole pair. Thus we can observe an absorption spectroscopy peak at the wavelength shorter than bulk material. When the excited electron returns to ground state, it emits a photon. The emission spectrum has a peak at a longer wavelength than the excitation spectrum because of the "Stokes shift". So we can tune the absorption and fluorescence property of QDs by changing its size. And to change the range of the optical property, we can change the composition of the QDs [23]. The imperfection on the surface of semiconductor crystal can trap electrons and disable them from recombination with holes to emit photons. To avoid this problem, a layer of another material on the surface of the QDs is introduced, which is called "shell". Most QDs are synthesized with surfactant on the surface, with the hydrophobic end pointing out. So the most commonly seen QDs have a core-shell-ligand structure.

QDs have promised to revolutionize the display technology, higher efficiency solar panel and biological labeling, which is already a happening reality[25]. However, the environmental danger of this material is also important. Cadmium is a common component of semiconductor QDs,

itself is a known toxic element and is responsible for the toxicity. Ron Hardman's review of QDs toxicity[10] provided the evidence of the toxicity. Such as the experiment with CdTe QDs coated with mercaptopropionic acid to rat pheochromocytoma cell. Cell death was observed with 10 mg/L concentration. It claimed at least part of the toxicity is induced by Cd. And the review also introduced Hoshino's experiment which showed the toxicity of the capping material on murine T-cell lymphoma cell at 100 mg/L. R. Kaegi *et. al.* [12] quantified the runoff of TiO_2 nanoparticles from exterior paint, showing the possible easy release of nanoparticles into the environment. In the aspect of nanoparticle aggregates in the water sediment column, Xiaoshan Zhu and *et. al.* [32] revealed that even with nanoparticles aggregated, it showed toxicity on zebrafish embryos and larvae, reducing the hatching rate, and introducing pericardial edema, which was unlikely caused solely by metal ion release from the aggregates. For the marine environment, direct toxicity of nanoparticles was observed at the concentration higher than 10 mg/L, and combined toxicity of nanoparticle with tributyltin (TBT) was showsn to be 20 times higher than TBT alone [33].

1.1.4 Scope of study and significance

This thesis is dedicated to model a natural scenario where QDs are effectively phase transferred into the aqueous phase, to characterize the role of model surfactant in this process, and to characterize the toxicity of phase transferred QDs to *Cyanobacteria* and microbial communities in anaerobic digesters.

Environmental scenario decides the property of the phase transferred QDs. Too often, people neglect the scenario but artificially create a unrealistic condition to test the toxicity which is not persuasive. Here we identify the a scenario which has not been reported before and see examine the biological impacts. Also, fatty acid soap has not been used as the model surfactant to study the phase transfer of the QDs. The thesis addresses this gap and shows that a weak model surfactant can effectively phase transfer QDs into water phase. Finally, the toxicity of the transferred QDs is studied.

1.2 Introduction to phase transfer of QDs

1.2.1 Origin of the problem: hydrophobic surface

High quality QDs are typically synthesized in organic solvents that makes them unsuitable in biological applications. In order to disperse the QDs in an aqueous phase, more compatible with biological applications, the hydrophobic surface must be rendered hydrophilic [14].

Hydrophobic QDs are used in solar panels, displays and lighting. These QDs may escape to the environment in the production, product cycle or at the end of product use. To investigate the natural transformation of water insoluble QDs into hydrophilic ones, it is important to review the current technologies to phase transfer QDs and look through their mechanism and the possibility of this mechanisms happening in the natural environment.

1.2.2 Technical solutions review

For phase transfer of QDs, there are three strategies: ligand exchange, silica encapsulation, micelle capture and polymer encapsulation. Each of them has both advantage and disadvantages, as discussed below.

1. The first strategy is a straightforward idea. The QDs are hydrophobic because of the hydrophobic ligands on the surface. So if replace these ligands with hydrophilic ones, the problem should be solved. To implement this method, the new ligand has one end attached to the exterior atoms on QDs, and has the other end being hydrophilic. The key to this method is the affinity of the terminal binding for the atoms on the QDs. The replacement can only happen when the affinity of this binding is higher than original. The advantage of this method is that, it generates the smallest possible QDs from the hydrophobic one. However, the disadvantages are also obvious. The exchange unavoidably disturb the surface atoms, which will introduce ion trap and reduce the quantum yield dramatically. The main bifunctional molecules are either easy to fall off the QDs over time due to chemical instability, expensive, or instable. The concentration of QDs during the reaction has to be low to avoid crossing-linking of the particles to nullify reactions between particles[31, 14].

2. Silica encapsulation. This is actually an extension of the first method. Ligand exchange with

silica precursors are the first step, which then cross-link to form a silica layer capturing the QDs. The second step provides the QDs more protection. The advantage of this method is that it improves both photostability and hydro-stability by providing an extra protection coating, and higher quantum efficiency. The disadvantage is that it will generate a bigger QDs by more than 10 times[31, 14].

3. Micelle capture. Some surfactants can form micelles when the concentration is high. In water solution, micelle is actually a special kind of aggregate. It has a hydrophilic surface outside, and hydrophobic surface inside. It might have some space in the center of the micelle. If the size of the space is right, it can be used to capture the QDs in water. Because the terminal bindings between the original ligands and the QDs are kept, the quantum efficiency mostly reserves. The interaction between the hydrophobic interior and the QDs alkyl chain offers extra protection to the QDs. And most of the surfactants in query are inexpensive. The disadvantage is that the size of the QDs is increased[31, 14].

Some instances of those technologies are specifically reviewed below due to their representativeness.

Gradual composition change of solvent mixture

According to Dominick[11], wrapping of the QDs with the polymeric micelles was induced by evaporation of Tetrahydrofuran (THF) and later by slowly evaporating water at temperatures below 10°C .

1. Disperse purified QDs in CH_2Cl_2.
2. Add polymer solution in MeOH (your polymer has to be MeOH soluble for that) Gradually evaporate CH_2Cl_2.
3. Add more MeOH.
4. Gradually evaporate CH_2Cl_2.
5. Repeat until you are sure there is no CH_2Cl_2 in MeOH.
6. Add small amount of water.

7. Gradually evaporate MeOH.

8. Add more water.

9. Repeat until you have water suspension of QDs.

There is a major difference between these two procedures: One only works with evaporating the water insoluble quantum dots (WIQDs) favorable phase, while the other is adding unfavorable phase during the procedure! The most important feature that makes the first one work is gradually changing the solution without any disturbs, while the second one breaks this harmony by introducing local unbalance making aggregations. Notice that before evaporation:

$$water : THF = 50 : 50$$

At this point, WIQDs are still stable. And after evaporation, there is enough unfavorable solvent to hold the final product. However, with the mixture of CH2Cl2:MeOH, though he did not mention the ratio, if there is enough MeOH at final stage, he would not add MeOH during the procedure. So a high initial ratio of unfavorable/favorable solvent is crucial for the success of this method. We can try out different combinations or we can try to find some data indicating that.

Oil-in-water emulsion

Fan, H. used evaporation-induced self-assembly coat QDs with amphiphilic agent[8]. The limitation of this approach is that only very strong surfactants that capable of forming micro-emulsion can be used as amphiphilic agent. Also, according to personal communication with Fan H., "The yield is low for QDs."

Solvent evaporation

Evaporation of QDs and surfactant solution in chloroform is also used to make surfactant micelles to encapsulate QDs. According to Pellegrino, T. *et al.* [19], they get a 100% yield of QDs with cross-linked enhanced surfactant encapsulation. With QDs produced with a similar schematics, [29] stained sub-cellular level targets specifically and efficiently. Based on the relative size of micelle core and QDs, [6, 5] also make a evaporation procedure that produces highly stable water soluble

QDs for bio-imagining. However, the performance of these methods is dependent on surfactant's ability to form suitable micelles.

Ring opening with QDs spontaneous transfer

Lees, E.E. and colleagues, developed an economical and easy method for coating the QDs in organic solvent and open the rings on the polymers to make the surface hydrophilic and transfer into water spontaneously[14]. The virtue of this method relies on the special ring structure of the surfactant, which can open and close as needed. This is not likely to happen in the natural water. The surfactants we use don't have such a special property either.

Mimicking natural process

Navarro used natural organic matter to assist phase transfer of quantum dots in organic phase into water[15]. Both ligand replacement and overcoating mechanisms have been observed during this process. This method is close to the natural scenario because it uses only the natural surfactant, and the reaction method is also very mild.

1.2.3 Overview of experimental approaches

Disperse dried QDs in surfactant solution

I first tried to directly disperse dried QDs in water. It is a straightforward idea: after discharging QDs into the environment, the organic solvent evaporates away leaving behind dried QDs. Subsequently surface water (with natural surfactants) could disperse these dried particles.

However, the results showed that majority of the QDs remained on the surface of the container. And even the transferred QDs, they were basically big aggregates.

Evaporation assisted phase transfer of QDs

The first idea did not succeed. So I began to look for a method most likely to successfully transfer the QDs from the organic to water phase. This method was inspired by Fan H.'s research[8].

This method involves first emulsifying the organic phase QDs into water using stirring / sonication with the addition of surfactants. Every drop of the organic solvent contains several QDs,

and the number is determined by the concentration of QDs and the size of the drops. Surfactant stabilizes the droplet by self-assembling at the interface of the drops and water. As the suspension heats, the drop evaporates and shrinks, forcing the surfactant at the interface to interdigitate with the alkyl ligand on the surface of the QDs. Stronger surfactants allow for smaller oil droplets, which can result in smaller phase transferred QDs aggregates.

The phase transfer efficiency is better by this method though it was still low. But it did show a positive relationship between the surfactant concentration and the phase transfer rate. This means in a scenario where QDs phase transferred into water with the assistance of evaporation can't be significant, which is not a dangerous scenario, either.

Micelle capture in organic solvent

The following line of thinking was inspired by Dubertret, B.'s work[6, 5]: Surfactants usually have a higher partition coefficient in an organic solvent than in water. If the solvent persists in the water for a while, it can concentrate the surfactant in the organic phase. As the organic solvent gradually evaporates, the surfactant can approach its CMC and form micelles to capture the QDs, thus completing the phase transfer process.

However, the result showed that it formed big flocculates, and the phase transfer efficiency was low with the surfactant we used.

Two phase interaction

In a relatively closed water body, the organic solvent is quite stable for a while, and the phase transfer happens in the interface of this solvent and the water surface, with the solvent beneath the water or above the water. The idea here is that setting up an experiment where both organic solvent phase and aqueous phase are stable. Provide minor turbulence and test the QDs in both phases.

The result showed that the phase transfer rate was low. Most of the QDs stayed in the organic phase.

Dissolve solvent to coat the QDs in surfactant solution

As the result shows, the phase transfer is not that significant. So is it the conclusion that the water insoluble QDs in the natural water is safe? In the real natural scenario, the quantity of solvent with

QDs should be relatively very small to the natural water body. Also, in most cases, in a open water body with turbulence, the solvent should spread out in the water fast and even with a very low solubility of the solvent in water, the solvent should dissolve away in the water when the solvent is very diluted as the solvent spread throughout in the water. Based on this scenario, we designed a new method to phase transfer the QDs into water.

The result showed that a high portion of QDs was transferred into the water phase. A positive relationship between the surfactant concentration and the phase transfer efficiency was observed when there is no fine foam during the reaction.

1.2.4 Summary of research objectives

1. Identify risks associated with various scenarios where water insoluble QDs can be effectively transferred into water in the presence of a weak surfactant in natural environment.

2. Characterize the relationship between the surfactant concentration and the phase transfer efficiency for these scenarios.

3. Characterize solution stability

4. Evaluate the toxicity of the phase transferred QDs on a model organism.

Chapter 2

Materials and Methods

2.1 Materials

2.1.1 Surfactants

Sodium hexanoate(SH), sodium decanoate(SD) and cetyltrimethylammonium bromide(CTAB) were bought from Sigma-Aldrich Corporation (St. Louis, MO). Critical micelle concentration (CMC) information for these surfactants is available in literature and online[27]. These surfactants were suspended in DI water.

Table 2.1: Property of Surfactants

	CTAB	Sodium Decanoate	Sodium Hexanoate
MW, Da	364.5	194.25	138.14
CMC, mole/L	0.001	0.14	2.2
CMC, g/L	0.3645	27.195	303.908
Concentration, mg/L	1000	2000	2000

Surfactant solution characterization Contact angle measurement was used to characterize the surfactant property.

2.1.2 Quantum dots (QDs)

Two products of CdSe/ZnS core/shell QDs were used. The first comes in the form of a toluene solution from Sigma-Aldrich, St. Louis, MO (#694630). These QDs were only used in the experiment for the section 1.2.3. The coating ligands are hexadecylamine. Because in the subsequent methods, chloroform is needed as the solvent and it is hard to get rid of toluene clearly. Solid QDs were purchased for the subsequent experiment ideals.

Table 2.2: Property of #694630 quantum dots

PROPERTY	SPECIFICATION
Related Categories	Core-Shell Type Quantum Dots
concentration	5 mg/ml in toluene
matrix active group	stabilized with hexadecylamine (HDA) ligand coating surface treatment
particle size	3.4 nm
bp	110 °C
density	0.865 g/ml at 25 °C
abs.	extinction/ 0.97 x 10-5 M-1cm-1
fluorescence	λ_{ex} 545 nm; λ_{em} 560 nm, FWHM $>$ 40 nm, quantum yield $\geq$30%

Solid QDs were bought from Ocean Nano Tech (Springdale, AR). The product name was "CdSe/ZnS Core/Shell Quantum Dot Solid" coated with octadecylamine. The physical characteristics are shown in table 2.3 as specified in its product sheet. These quantum dots were dissolved in chloroform and used in all experiments except that described in section 1.2.3.

Making a stock solution of QDs QDs was dissolved in a small amount of chloroform first. Then extinction coefficient method was used as described in section 3.1 to determine the concentration. Then the amount of extra chloroform solvent needed was calculated and added into the solution. The solution was measured again to confirm the concentration. The stock solution we used was of the concentration of 1.0 μM and was wrapped with aluminum foil to avoid light degradation.

Table 2.3: Analysis property of QSP-580-0010 quantum dots

PROPERTY	SPECIFICATION	METHOD
Quantum Yield	$> 50\%$	Integrating Sphere
Emission	577.5 nm	Fluorescence Spectroscopy
Full Width at Half Maximum	23 nm	Fluorescence Spectroscopy
Absorbance	563	Spectrophotometry

QDs characterization QDs dissolved in chloroform was characterized using absorption fluorescence spectroscopy (figure 3.1) and dynamic light scattering (figure 3.2).

2.2 Analytical instrumentations

2.2.1 Absorption fluorescence spectroscopy

A micro-plate reader, Model Infinite m200 PRO NanoQuant, from Tecan Group Ltd (San Jose, CA) was used for fluorescence reading and absorbance measurement. A quartz cuvette (Fisher Scientific Inc., 14-385-910A) was used for absorbance measurement with QDs in chloroform solution. Because chloroform can dissolve polystyrene, plastic cuvette was avoid. Thermo Scientific Nunc Flat Bottom 96-well polystyrene transparent plates was used for aqueous measurements. One of the key optical properties of QDs is that they have wide absorption bands, but narrow emission bands. Furthermore, emission is in the visible spectrum. Hence, quantum dots are widely quantified by means of relative absorbance and emission readings. According to Yu and his co-workers [30], the specific absorbance spectrum of quantum dots can also be used to determine the diameter of QDs (equation (3.1) and (3.2)), and the concentration of QDs in the solvent solution(equation (3.3)).

Fluorescence spectroscopy was adopted for fluorescence spectrum analysis. As explained in the introduction chapter, the recombination of electrons and holes on QDs produces emission of photons from QDs. The emission of the QDs in a solution comprises a fluorescence spectrum. First, the detection of a fluorescence peak can be used as evidence of phase transfer. Secondly, the full width at half maximum (FWHM) can be used as an indicator of the homogeneity of QDs. Third, the shift of the emission maximum can be used to estimate the integrity of QDs[16].

2.2.2 *Dynamic light scattering*

Dynamic light scattering was used to obtain the size distribution of QDs in chloroform solution, and characterize the phase transferred QDs in aqueous solution. Malvern Nano ZS (Worcestershire, United Kingdom) was used for Dynamic Light Scattering (DLS) analysis. This instrument is capable of detecting particles from 0.6nm to 6 um with a 532 nm laser.

DLS size measurement is based on two relationships. One is the relationship between diffusion speed and diffusion constant. The other is about diffusion constant and spherical particle radius. All particles display Brownian motion and scatter incident light corresponding to the particles' motion. The scattering pattern of light intensity can be detected by an autocorrelator, i.e. a device used to measure the scatter pattern of light with itself after a small time interval. Large particles have slower motion, which results in a greater correlation between scatter patterns measured in time. Similarly, smaller particles have smaller autocorrelation. The mathematical relationship between the autocorrelation function and the particle size is stated below:

Relationship between diffusion speed and size First, by tracing light intensity in a time series, second order autocorrelation value of the intensity is obtained.

$$g^2 = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2}$$

Where

g^2: second order autocorrelation function

I: light intensity

τ: delay time

Using Siegert equation to calculate first order autocorrelation from the second order autocorrelation.

$$g^1 = \sqrt{\frac{g^2 - 1}{\beta}}$$

Where

g^1: first order autocorrelation function

β: correction factor

Then based on equation (2.1), Γ can be estimated.

$$g = exp(-\tau\Gamma) \tag{2.1}$$

Where

Γ: decay rate

Decay rate is a reflection of the diffusion speed of a particle. The relationship can be described by equation (2.2).With equation (2.2), diffusion coefficient, a value characterizing the diffusion speed can be calculated.

$$\Gamma = q^2 \times D_t \tag{2.2}$$

With

$$q = 4\pi sin(\theta/2)\frac{n_0}{\lambda}$$

Where

D_t: diffusion coefficient

q: wave vector

n_0: refractive index of the sample

λ: incident laser wavelength

θ: angle between detector and the sample cell

Stokes-Einstein equation: relationship between diffusion speed and small particle size

$$D_t = \frac{k_B T}{6\pi\eta r} \tag{2.3}$$

Where

k_B: Boltzmann's constant

T: absolute temperature

η: viscosity of the solvent

r: spherical radius of the particle

With equation (2.3), r, radius of the particle, can be obtained.

2.2.3 Contact angle measurement

We attempted to use contact angle measurement to characterize surfactant solutions. Contact angle is commonly used to characterize the surface hydrophilicity [7]. A surfactant can change the surface tension of a the solution, which would result in the change in the contact angle, θ as it shows in figure 2.1. Contact angle measurements were conducted on VCA Optima (AST products, Inc, Billerica, MA).

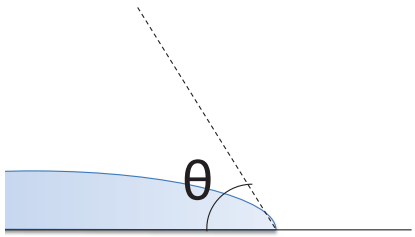


Figure 2.1: Contact angle measurement

2.3 Methods

2.3.1 Dispersal of dried QDs in surfactant solution

5 μl QDs toluene solution was dispensed into a 2.0 ml polypropylene centrifuge tube. The tube was left open and the toluene solution was air-dried in a chemical fume hood until no liquid was visible on the surface of the QDs. This step took about 10 m. 1 ml of surfactant solution was added into the tube. The tube was closed and shaken for 20 minutes. A pipette was used to take sample from tube and the fluorescence of the sample was read at an excitation and emission wavelengths of 400 and 580 nm respectively. This would be the fluorescence value in the water solution. The

water solution was drained in the tube and dried for 30 minutes under room temperature. 1 ml of toluene was added into the tube. The tube was shaken to release the QDs from the wall and the QDs were re-suspended in the toluene. Sample of the toluene solution was taken. This fluorescence value would reflect the amount of QDs left on the wall after the interaction with surfactant.

2.3.2 Evaporation assisted phase transfer of QDs

20 ml surfactant solution was added into a 150 ml beaker. A magnetic rod of a suitable size was put into the beaker. The beaker was located in the center on the magnetic stirrer of the hotplate. It was stirred at 900 rpm. 5 μM QDs chloroform solution 1 ml was injected at a stable speed (because a normal pipette was used for this injection, the exact speed is unavailable. But the estimation would be around 0.5 ml/s). Preheat the beaker at 100 °C degree for 5 minutes. The stirring speed was adjusted to 1200 rpm. The hotplate temperature was adjusted to 200 °C degree. It was heated and stirred for 10 minutes. The real temperature in the beaker was 80 °C degree, while the boiling point of chloroform was 61.2 °C degree. The sample was taken after the solution was cooled down.

2.3.3 Micelle capture in organic solvent

The idea of this method was based on the difference in solubility of the surfactant and QDs. At the beginning of the process, both surfactant and QDs should be dissolved in the solvent. As solvent evaporated, QDs remained suspended, but the surfactant began to form micelles. These micelles would capture the QDs if their diameter was larger that that of the QDs. Consequently, at the end of the experiment, when all solvent had evaporated, each QD should have be covered by surfactant individually.

This scenario is possible in the environment, where the QDs solvent can gather surfactant from natural water due to the high partition coefficient of the surfactant between solvent and water and subsequently cause the dispersion of QDs in water.

The procedure for this experiment was as the following: Surfactant was dissolved into the chloroform until saturation, so that the highest possible concentration of surfactant was achieved, which had the best capture performance. In 20 ml surfactant solution, 1 ml 1 μM QDs was added into it. The solvent was evaporated at a room temperature for 1 hour. 1000 mg/L surfactant solution 1 ml was added, and sonication/stirring was applied. The fluorescence and size of aggregates was

measured.

2.3.4 Interaction between two phases

This method follows the idea described in section 1.2.3. 2 ml of QDs was added in chloroform into a 7 ml glass vial. 2 ml of surfactant solution was added into the vial. The vial was wrapped with aluminum foil (it would shield the light from degrading fluorescence efficiency) and shaken gently. The mixture was transferred into a separator funnel and separated into the two phases before sampling. Both the water phase and the organic phase are sampled.

2.3.5 Gradual dissolution of QDs in surfactant solution

Preparation of QDs stock solution and characterization QDs were first suspended in chloroform (approx. 0.75% ethanol as preservative and the certified ACS reagent grade is $\geq 99.8\%$). There were several reasons for using chloroform as the solvent. QDs were dispersed in chloroform. Additionally, during the reaction, we wanted to avoid oxidization of the QDs surface by minimizing the contact of QDs with air. Chloroform has a higher density than water, which was better than solvent like hexane (0.65 g/cm^3) from the perspective of avoiding contact with air in a mixture. Additionally, chloroform has a relatively low boiling point (61.2 °C) and can be easily volatilized by extended stirring and heating.

Using the method described by Yu[30] and equation (3.2), the concentration of stock solution was adjusted to 1.0 μM as described in paragraph 2.1.2. A diluted solution was used for size distribution analysis with dynamic light scattering analysis. 0.1 ml stock solution was added into the quartz cuvette, and diluted with 0.9 ml chloroform.

Operations to phase transfer QDs A Pasteur pipette was clamped in a vertical orientation. The height of the pipette was adjusted so that the tip was just above the brim of a 200 ml beaker. The beaker was centered on the stirring hotplate. Approximately 20 ml water was added into the 200 ml beaker. A magnetic rod was dropped into the beaker whose length is about $\frac{2}{3}$ of the beaker's diameter in it. Stirring was started. The beaker was moved around on the surface of the stirring hotplate until the fluid swirl achieved a uniform height around the wall of the beaker. The location

of this beaker was marked for future reference.

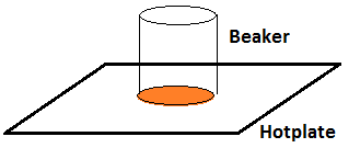


Figure 2.2: Marking beaker location

To drop the chloroform at the same location in the beaker, a special cap with a pipette position template was used. Make a cap on the beaker as it shown in figure 2.4. It was a metal cap whose diameter slightly bigger than the diameter of the beaker. A slot was cut on the metal cap, which was a little boarder than the diameter of the tip of pipette.

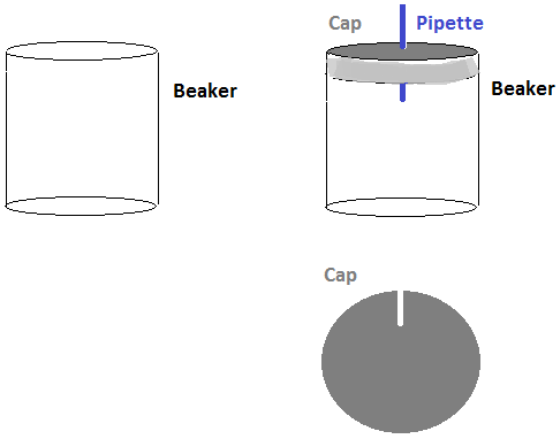


Figure 2.3: Locate the pipette above the beaker

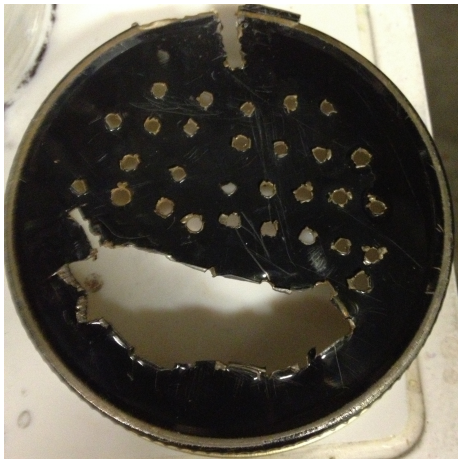


Figure 2.4: The metal cap

Ensure a consistent positioning of the pipette tip on the beaker and the beaker on the hotplate.

Because the change of the pipette position will lead to the different spreading speed of the chloroform speed in the beaker and different location of beaker on the hotplate will introduce different stirring speed.

Set up a syringe pump and connect the outlet of the pump to a Pasteur pipette through a tube. To prevent leakage of the chloroform from the pipette tip, the inside surface of the tip needed to be rinsed with chloroform. The Pasteur pipette was refilled and emptied with chloroform for several times until no chloroform dropped while the pump was off. Fill the pipette with 1 ml of chloroform. Then the beaker was relocated under the pipette. The stirring was turned on first. Then the pump was started at the desired flow rate and began timing the process. Stop the pump when a desired amount of chloroform have been dispensed. To eliminate the chloroform completely, stirring was continued for 15 minutes after stopping the pump. The magnetic rod was cleaned. The magnetic rod was soaked in high concentration hydrochloric acid for 5 minutes to get rid of QDs coated on the surface. It was taken out and immersed into ethanol solution to remove any chloroform residue on the surface. It was flushed with DI water and air-dried. Ultrasonic washer was used to clean up the coated QDs on the surface for 45 minutes sonication. Then beaker was flushed with DI water and air-dried.

2.3.6 Toxicity of phase-transferred quantum dots in Synechococcus elongatus

First, the toxicity of chloroform residue in the phase transferred solution should be estimated and eliminated. 6 ml chloroform was injected at the flow rate of 50 ul/min into 20 ml 1000 mg/L sodium decanoate solution. The solution was stirred at 900 rpm. After the reaction, a marker was used to label the height of solution in the beaker. 550 °C degree hotplate temperature was applied without stirring for certain minutes as indicated in the specific experiment. After heating, DI water was added so that the solution resumed to the label. Absorbance measurement was taken after cooling down. A certain amount of the solution was added into cyanobacteria. The absorption of cyanobacteria was measured at wavelength 750 nm.

Chapter 3

Results and discussion

3.1 Characterization of QDs

3.1.1 Spectroscopy

QDs were dissolved in chloroform at a concentration of 0.1 μM. Fluorescence and absorbance spectra were measured with the Tecan spectrophotometer. Figure 3.1 shows that fluorescence and absorption spectra of the QDs that came in solid form. The excitation and emission wavelengths were 400 and 580 nm respectively.

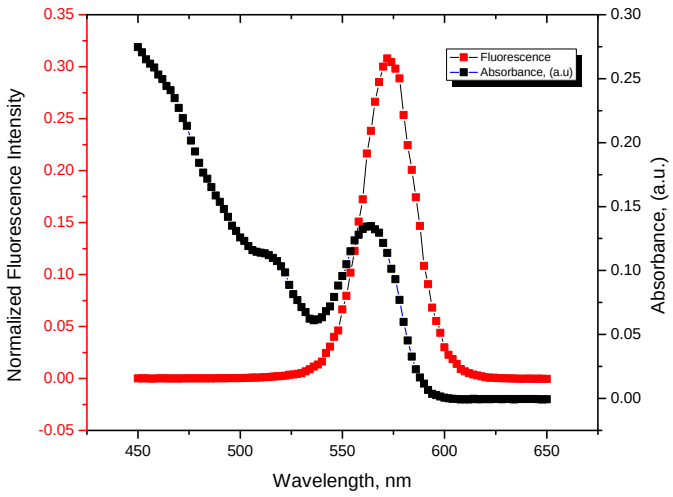


Figure 3.1: Absorption and fluorescence spectra of octadecylamine-coated CdSe QDs in chloroform

Diameter of the CdSe QDs nanocrystal core is estimated to be 3.4 nm. The first absorption peak, λ, is at 564 nm. According to Yu W.'s study [30], the diameter of the CdSe QDs core diameter can be calculated from equation (3.1).

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - 0.4277\lambda + 41.57 \tag{3.1}$$

For CdSe, extinction coefficient can be obtained from equation (3.2). The result is about 145079 $L/molcm$.

$$\epsilon = 5857D^{2.65} \tag{3.2}$$

Concentration of the QDs can be calculated from equation (3.3).

$$A = \epsilon CL \tag{3.3}$$

With

$$A = A_m(fwhm)_{UV}/K \tag{3.4}$$

Where

A**:** absorbance at the first exciton absorption peak

A_m**:** the measured absorbance

C**:** concentration of QDs, mol/L

$fwhm_{UV}$**:** Full width at the half-maximum on the long wavelength side of the first absorption peak

K**:** average $fwhm_{UV}$

L**:** path length of the cuvette, cm

To make a solution of desired concentration, add or evaporate the chloroform to achieve the concentration in query.

3.1.2 *Dynamic light scattering*

Add 0.1 μM of QDs chloroform solution in a screw top glass cuvette and take a measurement with dynamic light scattering.

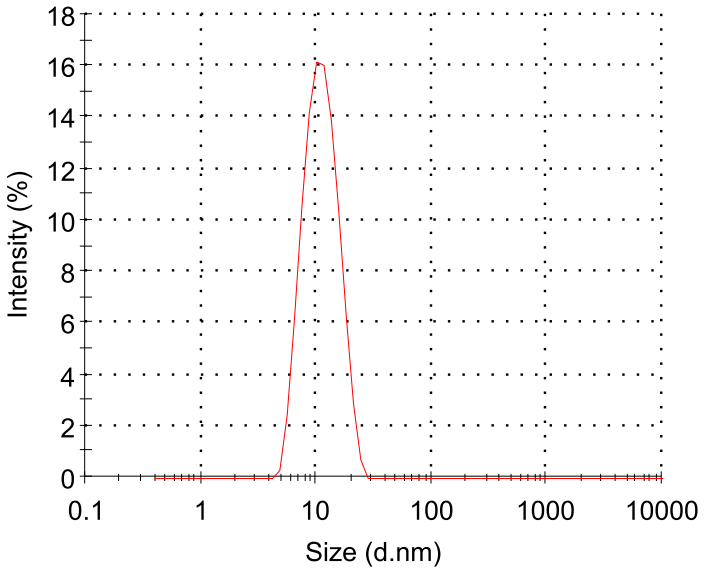


Figure 3.2: Size distribution of solid QDs dissolved in chloroform, 0.7 μM

Figure 3.2 is the size distribution analysis result from dynamic light scattering by light intensity. In figure 3.2, it shows that the hydrodynamic diameter of QDs is about 10 nm. Note that the diameter of the nanocrystal core is about 3.4 nm based on the previous estimation. The shell and ligands over the core add to the diameter of the QDs. And because of the hairy structure and the viscosity of the chloroform, it is understandable that the hydrodynamic diameter is greater than the real diameter of the particle.

3.2 Fluorescence of QDs vs. concentration of QDs

Make a series of different concentrations of QDs in chloroform and test the fluorescence reading at 580 nm with 400 nm exciton laser.

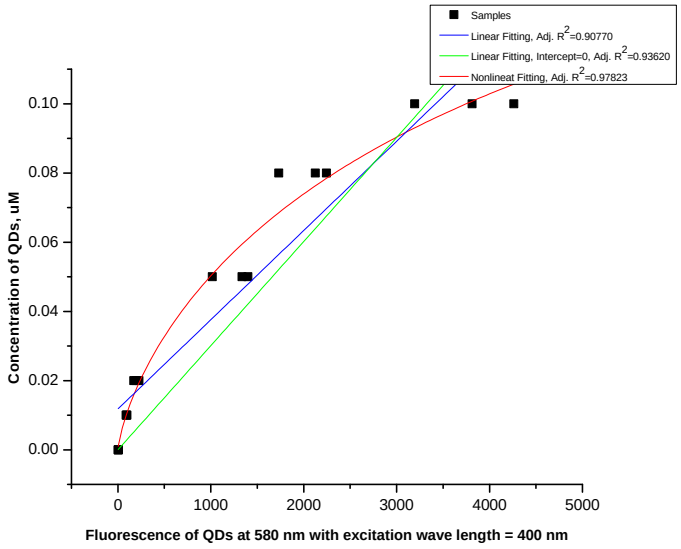


Figure 3.3: Fluorescence vs. concentration of QDs

Figure 3.3 illustrates a positive relationship between fluorescence of QDs and their concentration in chloroform. In order to use this relationship to estimate the concentration of QDs, three fittings are adopted. According to the $Adj.R^2$ value, the third fitting method fits the data the best. Especially for the low concentration part (below $0.05uM$), which is of our interest, the third method fits the plots much better than the first two methods. So the third fitting is adopted to represent the relationship between concentration of QDs, and their fluorescence. In the subsequent experiment, this curve is used to estimate the concentration of QDs in water phase based on the fluorescence.

3.3 Characterization of surfactant

The first step to measure the contact angle of different concentrations of surfactants is to decided which substrate to use. Usually, the one with higher hydrophobicity for the aqueous liquid is the choice. If it is a too hydrophilic surface, the solution drop will expend out of the camera view. Due to the limit of resources, the materials of consideration is only glass and polystyrene. In figure 3.4, it shows that polystyrene surface has a much higher contact angle than glass surface.

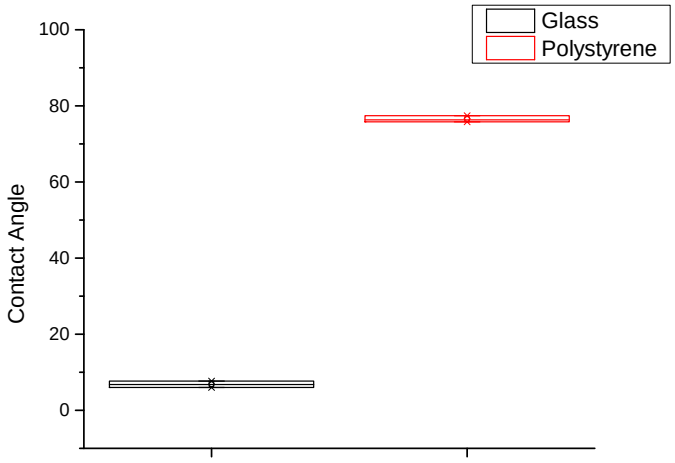


Figure 3.4: Contact angle measurement with glass and polystyrene surfaces

With polystyrene as the substrate, contact angles of difference concentrations of sodium decanoate has been measured.

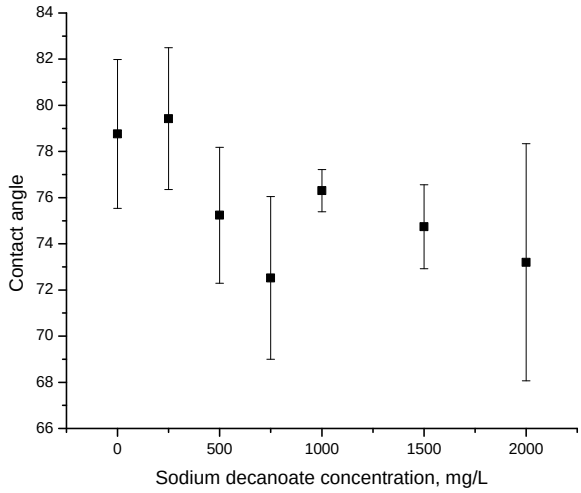


Figure 3.5: Contact angle measurement with different concentrations of sodium decanoate

However, in figure 3.5, it shows no relationship between surfactant concentration and contact angle value as expected. The first problem with this is that the contact angle measurement is usually designed to characterize the surface difference rather than the solution difference. As we see in figure 3.4, it made a sharp distinction between these two materials. Second problem is that, the

substrate we have is highly reflective which makes the equipment hard to measure the contact angle automatically. The measurement is carried out by human decision. A typical measurement picture is shown in figure 3.6. The two ends of the chord was identified with visually. And a third point on the arc was also picked by naked-eye.

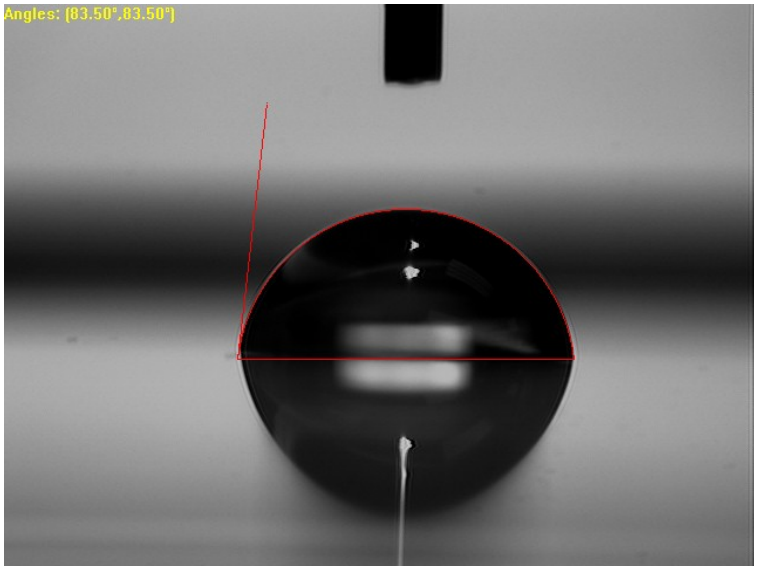


Figure 3.6: Contact angle measurement picture

3.4 Surfactant solution interaction with dried QDs

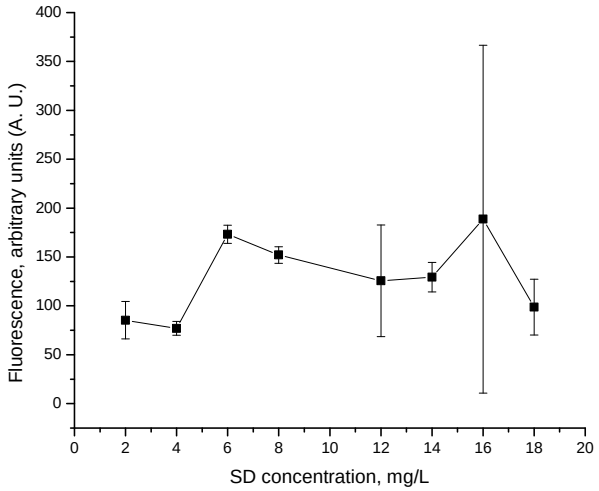


Figure 3.7: Sodium decanoate concentration vs. fluorescence in water phase with method one

Result and discussion In figure 3.7, no reasonable relationship between surfactant concentration and QDs phase transfer can be identified. Also, the standard deviation is very large, indicating the big aggregates of the QDs.

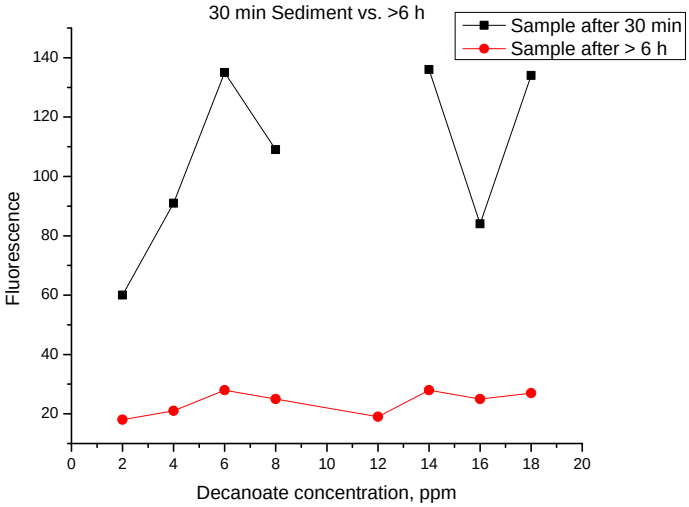


Figure 3.8: Precipitation of QDs from water phase in six hours

Figure 3.8 shows the fast precipitation speed. In six hours, majority of the QDs had settled out from water. That meant most of the QDs in the water phase were big aggregates. This phenomenon helps to explain figure 3.7. Because the QDs in water was basically big aggregates, which was not uniform, the standard deviation was very big and it made samples hardly represent the QDs in the whole solution. Considering its low mobility and lack of bio-availability, this was not a dangerous scenario to the natural system.

The QDs in water were in big aggregates can be further confirmed. Visible QDs aggregates were observed in figure 3.9

Figure 3.9: QDs aggregates in the tube under UV light illumination

After observation of the water phase, figure 3.10 shows the QDs remained on the wall of tubes.

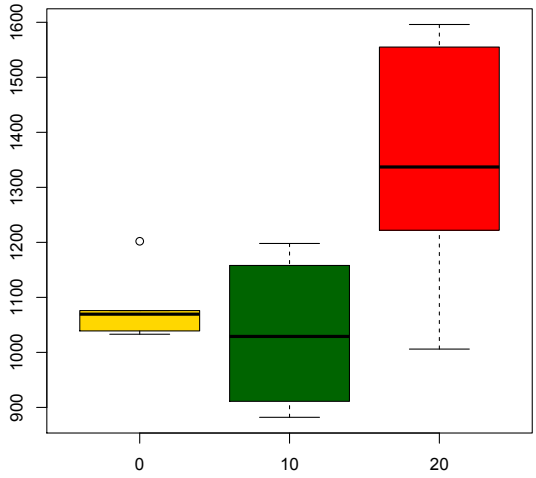


Figure 3.10: Fluorescence left on the tube after interaction with surfactant VS. concentration of sodium decanoate, ppm

By comparing figure 3.7 and figure 3.10, it was easy to see that majority of QDs had been left on the wall of tubes (roughly 90%). Also, notice that for 20 ppm of sodium decanoate, even more QDs had been left on the wall than the ones with lower concentration. This meant the effect of surfactant was obscure, or the QDs were too much strongly attached to one another.

This strong interaction between the QDs might be explained by two facts.

1. Toluene residue. The first one is that, due to the special hairy surface of the dots, toluene residue on the surface will form a concave liquid surface. Because of the distance between ligand on the surface is below one nanometer, the radius of the concave surface is at a similar scale. This will introduce capillary condensation effect, which makes the evaporation

extremely hard. Thus, there is always toluene residue even evaporating the volatile solvent for hours. And this remnant acts like a glue between the QDs.

2. Van der Waals force. The evaporation of the toluene compresses the space of the QDs, and narrows the distance between QDs. Eventually, the stabilizing ligands on dots interdigitate with one another (see 3.11). And through Van der Waals force between these ligands, QDs tightly bond with each other.

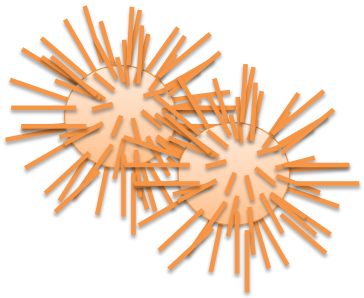


Figure 3.11: Inter-digital interaction between QDs through Van der Waals force

Conclusion

1. Under this scenario, where solvent evaporates before the interaction between surfactant solution and water insoluble QDs, minority of the QDs aggregates into big flocculates in water phase. And settle down in a short time. They precipitate out in hours.

2. Under the turbulence of surfactants solution, those aggregates hold to the solid surface firmly, that about 90% of the aggregates stay still.

3. In both cases, QDs lose the mobility and bio-availability. This is not a dangerous scenario we are trying to find.

3.5 Emulsification of QDs solution in surfactant solution

Result and discussion Heating QDs solution in CTAB solution transfered QDs into water homogeneously, which can be proved by figure 3.12. Approximately 0.75 μM QDs chloroform solution was used. Due to the low fluorescence value of the phase transferred QDs, the gain of Tecan had been changed to 200 to make the result visible. Figure 3.12 shows that, higher concentration of

surfactant can phase transfer more QDs into water phase. However, the phase transfer efficiency is still very low.

Another problem with this method is that the heating process is rare in natural environment. This result has little environmental relevance.

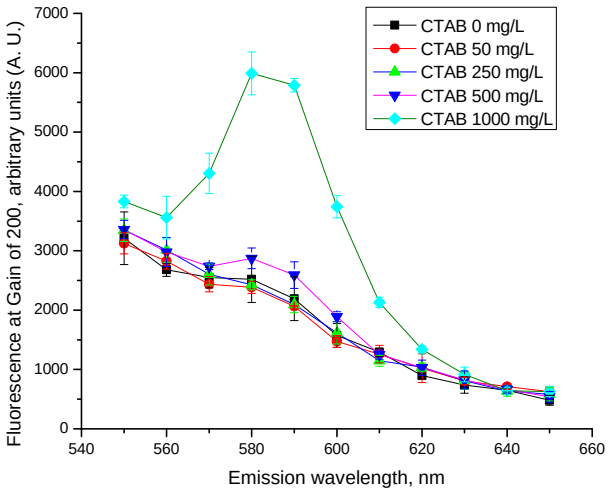


Figure 3.12: Phase transfer of QDs with difference concentration of CTAB solution

Conclusion Even though this method has little environmental relevance, the mechanism which transfers the QDs into water is interesting. After added into surfactant solution, the QDs chloroform solution is broken into tiny oil drops. If the surfactant can reduce the surface energy to a enough low level, the size of the oil drops can be so small that each of them contains only couple of QDs. In the interface of those tiny oil drops and water, surfactant is concentrated in the oil drop with hydrophobic alkyl chain oriented towards to the QDs. As the solvent evaporates, those alkyl chains interdigitate with the alkyl chains of the ligands on the QDs surface, leaving hydrophilic end outside of the QDs. Thus, the surfactant transforms the hydrophobic QDs into hydrophilic ones. The successful method was inspired by this method.

3.6 Micelle capture of QDs in organic solvent

Result and discussion The difficulty with this idea is that it needs to be a perfect match where:

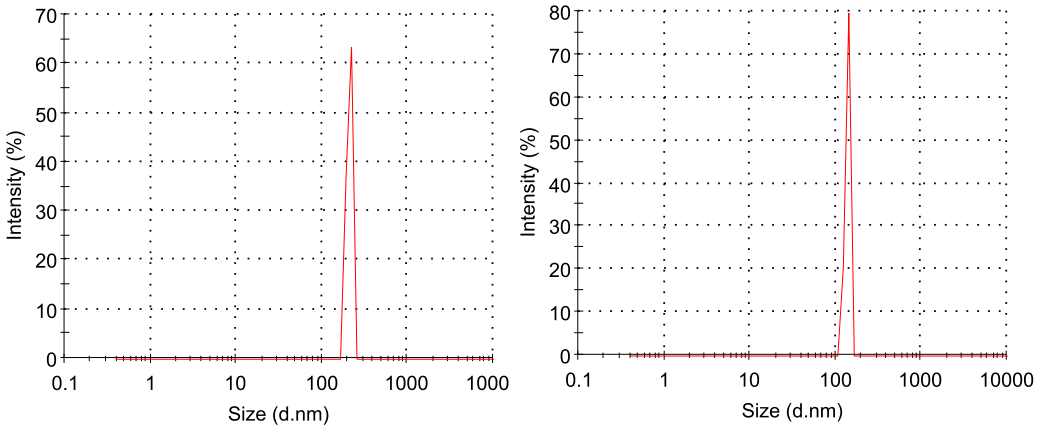
1. The QDs should be highly soluble in the solvent. At least, at the CMC of the surfactant, the

QDs should be able to dissolve in the solvent.

2. Surfactant should have a high solubility in the solvent. If only the concentration of the surfactant is high enough, the number of micelles formed by this surfactant was big enough for capturing a big amount of QDs.

However, we have only fatty soap salt and CTAB as the surfactants combinations. And we have no time to try out all kinds of solvent. We have no access to Hansen solubility data either to see how soluble each surfactant is in all solvents. We only tried the experiment with chloroform, hexane and ethanol.

The only surfactant among those four that is highly soluble in solvents like chloroform and hexane is CTAB. However, it showed that the one evaporating with CTAB in the QDs chloroform solution has a greater aggregate diameter than then one without CTAB.



(a) QDs chloroform solution evaporated with CTAB

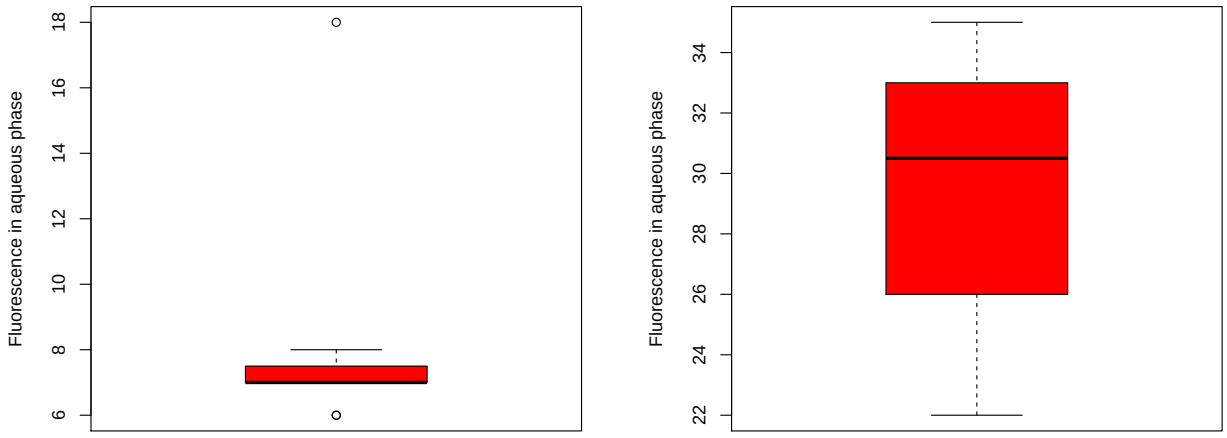
(b) QDs chloroform solution evaporated without CTAB

Figure 3.13: Phase transfer results with QDs from evaporating chloroform solution

Conclusion Because the objective of this thesis was finding the most dangerous scenario for QDs, and this method did not provide a good potential, it was stopped at this point. Nevertheless, this experiment provides information of that for solvent staying in water, even when it gathered high concentration of surfactant, it would not be a danger to phase transfer nanoparticles effectively.

3.7 Partition of QDs between solvent and water phase

Result and discussion After nine days' interaction between 10 ml 0.1 μM QDs and 10 ml 1000 mg/L sodium decanoate solution, little QDs had been transferred into the water phase.



(a) Fluorescence in the water phase after 9 days of interaction, sodium decanoate as surfactant

(b) Fluorescence in the water phase after 9 days of interaction, CTAB as surfactant

Figure 3.14: Comparison of phase transfer fluorescence after 9 days of interaction between sodium decanoate and CTAB

As a comparison, CTAB with the same concentration has been tested. The result is shown in 3.14b. As it showed, still the QDs phase transferred into water was low.

Actually, by looking at the interface between water and chloroform, flakes of aggregates were presented.

Conclusion Compared with Navarro's result[15] with a low concentration of humic acid as the surfactant, the phase transfer rate was very low. Large molecules like humic acid has a better performance in phase transferring nanoparticles into water phase than small surfactants, like fatty soap salt. This might suggest that if there is any effect with these module surfactants we have on phase transferring QDs, it could be a even more dangerous case in the natural water bodies with large natural surfactant molecules like humic acids and fulvic acids. Also, it gives the null

result about the experiment idea or hypothesis. Module surfactant can't phase transfer the QDs into water phase by this method or mechanism. Given the objective is to find a most dangerous scenario and to identify the effect of surfactant, this method is not worthy of further work.

3.8 Gradual dissolution of QDs in surfactant solution

3.8.1 Evidence of effectiveness and mechanism

Figure 3.15 provided evidence of the benefit of gradual injection. Group one in figure 3.15 was the emulsification method, heating and evaporating emulsified QDs solution. And group two was the new method. Both groups were treated with 2 ml 0.75 μM QDs, 900 rpm, 20 ml 1000 ppm sodium decanoate solution. Photoluminescence was measured at 580 nm with 400 nm exciton wavelength.

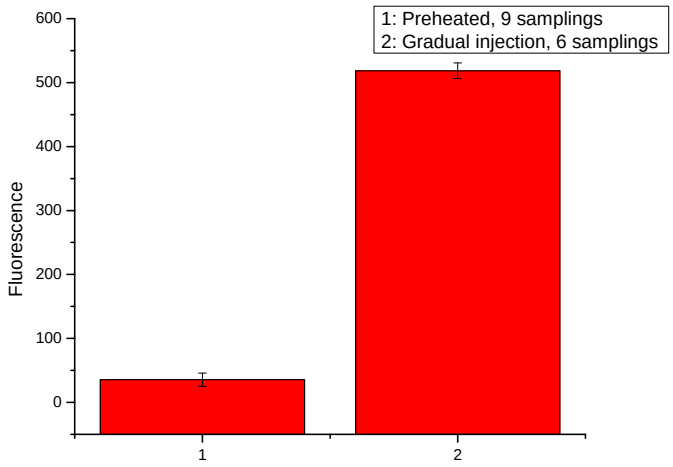


Figure 3.15: Heated sodium decanoate solution vs. normal surfactant solution with gradual QDs chloroform solution injection

Four treatments are used to test the effect of injection rate and heating.

1. 1 ml QDs chloroform solution was added in one shot. And it stirred for 10 minutes.
2. It added 0.2 ml QDs solution every one minutes for 4 minutes. And it continued with stirring for another 6 minutes.
3. QDs solution was added into the beaker at a even flow rate over 20 minutes.

4. 1 ml of QDs solution was added in one shot into the heating surfactant solution (200 C as the hotplate setting temperature, but the temperature of the solution was always below 80 C due to the fast evaporation eliminating the heat).

All of the experiments were setup with 1000 mg/L sodium decanoate solution 20 ml, and stirring at 900 rpm. The result is shown in figure 3.16. The comparison is also with a time difference to eliminate the possibility of the stirring time difference effect and to see the stability. As it shows in figure 3.16, the gradual dissolving method has the highest phase transfer efficiency among the four groups. Also, the efficiency is also higher than any previous experiment result. The performance is about 6 times better than any other group.

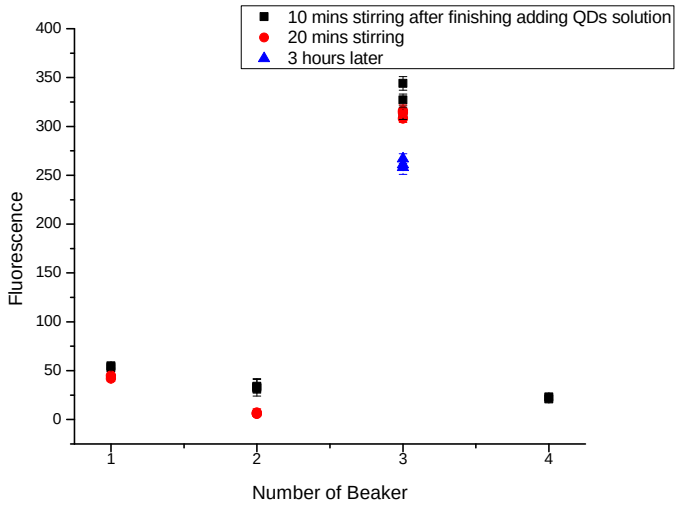
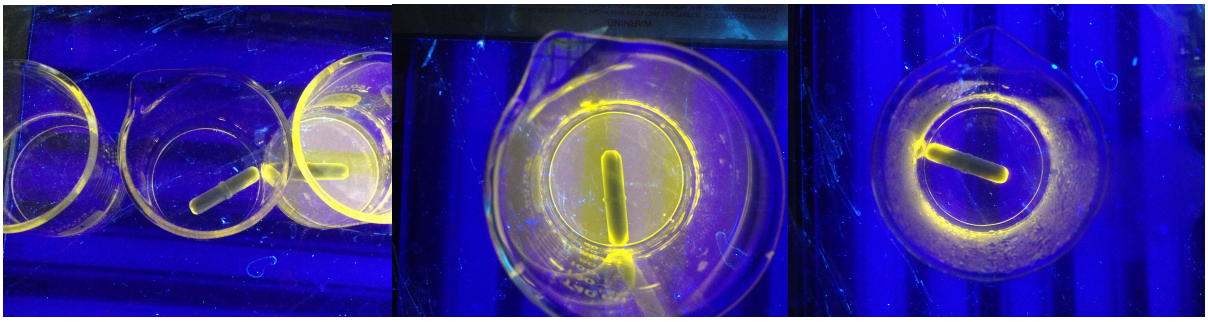


Figure 3.16: Fluorescence of the water phase after injection for four beakers

3.8.2 Evidence of the advantage of gradual injection

In figure 3.17, it shows the picture of the beakers under UV illumination after 3 hours of settlement. As it shows, only beaker # 3 had fluorescence homogeneously distributed in the water phase. The first two beakers had no fluorescence as all. And the fourth beaker had only visible fluorescence on the magnetic rod and the wall of the beaker. This picture confirms that this method had successfully phase transferred the QDs into water phase. And the QDs in the water phase were mostly in small aggregates.

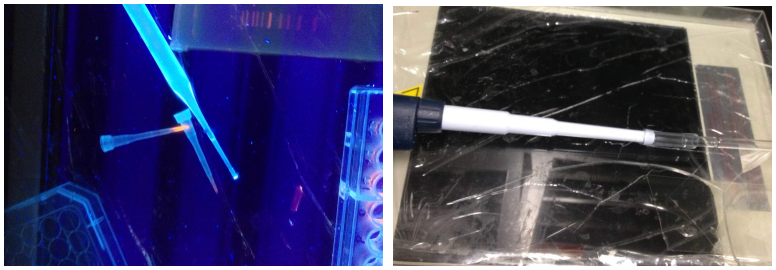


(a) Beaker # 1, # 2 and # 3 (b) Beaker # 3 (c) Beaker # 4

Figure 3.17: Comparison between different injection method among four beakers: one shot, 0.2 ml every one minute, drop by drop, and one shot plus heating

3.8.3 Experimental evidence of the essential details in the experiment

Tips One important detail about the experiment is that, the QDs can easily stick to a polypropylene tip and introduce extra error into the sampling. But with glass tip, this can be avoid.



(a) Polypropylene tips attached with QDs and glass tips clean of QDs, after sampling

(b) Usage of Pasteur pipette in replacement of expensive professional glass tip

Figure 3.18: Glass pipette tips

As it shows in figure 3.18a, the glass tip got nothing left while the polypropylene tip was strongly attached by QDs. And figure 3.18b shows a little trick here. Since the commercial standard glass tips for pipette is expensive, we avoid buying it by connecting a Pasteur pipette through a latex tube to the pipette.

Beaker location on the hotplate and the position of the tip Figure 3.19 explains the advantage of the method described to control the beaker, tip and hotplate relative locations in the method section. The standard deviation was much lower for the controlled one compared to the null one. Also, it had a higher phase transfer efficiency.

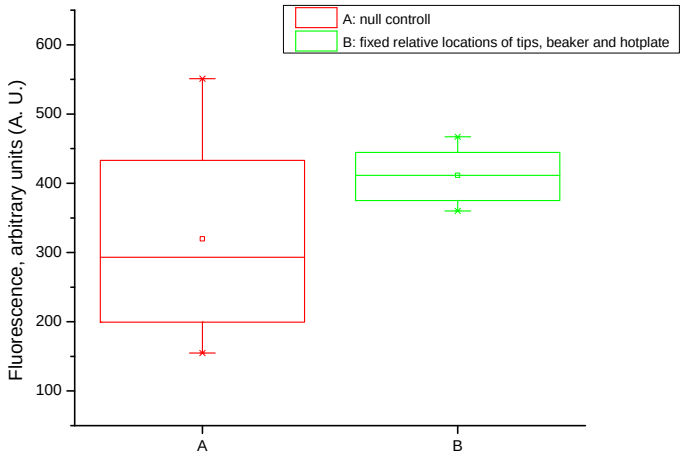
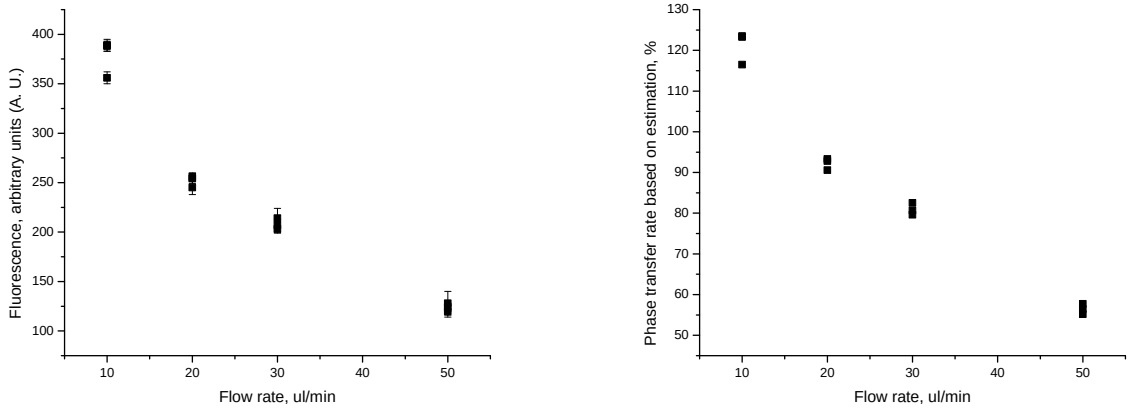


Figure 3.19: Difference between null control and fixed relative locations of tip, beaker and hotplate

Leakage of the QDs solution Because the weight of chloroform is much very high, it is easy for the chloroform running out of the tip with the pump off or it adds to the setting flow rate. As it shows in figure 3.20b, the flow rate is essential.

3.8.4 Flow rate vs. phase transfer efficiency



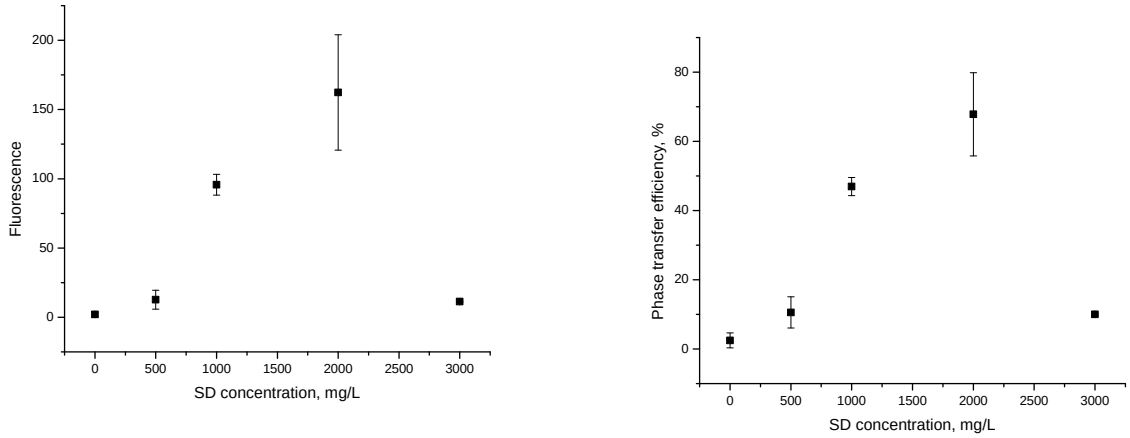
(a) Flow rate vs. fluorescence of aqueous phase

(b) Flow rate vs. phase transfer efficiency

Figure 3.20: Phase transfer of QDs with different flow rate, 0.6 ml 0.75 μM QDs, 900 rpm, 20 ml 1000 ppm sodium decanoate solution

In figure 3.20a, it shows the relationship between fluorescence in water phase and the flow rate of QDs solution into the beaker. As it shows, the lower flow rate, the more QDs transferred into water phase. In figure 3.20b, the phase transfer efficiency was estimated by the fluorescence of the water phase, based on the relationship discovered between fluorescence and the concentration in previous section. Here we see the trend clearly. Because the relationship was in chloroform solution with monodispersed QDs, which was different from the QDs aggregates coated by surfactant in the water phase, the highest rate went over 100%. This problem can be solved easily with atomic spectroscopy.

3.8.5 Surfactant concentration vs. phase transfer efficiency



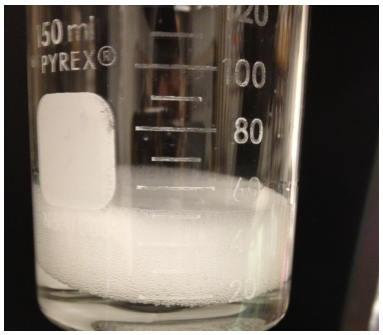
(a) Concentration of SD vs. fluorescence of aqueous phase

(b) Concentration of SD vs. phase transfer efficiency

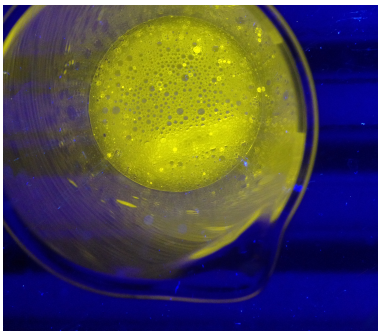
Figure 3.21: Phase transfer of QDs with different concentration of sodium decanoate, 0.6 ml 0.75 μM QDs, 900 rpm, 20 ml surfactant solution

Phase transferred QDs continued to increase as the concentration of sodium decanoate raised. Until at the concentration of 3000 mg/L, the trend suddenly turned around. It was caused by the extensive fine bubbles of solution with 3000 mg/L concentration. Between 2000 mg/L and 3000 mg/L, there is a turning point, crossing which fine foam accumulates dramatically. And under the UV, it is easy to see that chloroform drops are not dissolved as expected. They are attached to the bottom of the foam, and fails to dissolve and evaporate quickly.

(a) Sodium decanoate 2000 mg/L, no foam



(b) Sodium decanoate 3000 mg/L, fine foam on surface



(c) Sodium decanoate 3000 mg/L under UV

Figure 3.22: Phase transfer of QDs with different concentration of sodium decanoate, 0.6 ml 0.75 μM QDs, 900 rpm, 20 ml surfactant solution

3.8.6 Volume of solution vs. phase transfer efficiency

Figure 3.23 shows the result for continuously adding QDs solution into a stirring sodium decanoate solution. As the result indicates, the fluorescence of QDs in the solution continues to increase almost linearly to the volume of QDs solution added. And the Phase transfer efficiency decreases by about 30%. Because as the surfactant coated on the surface of QDs, the amount of surfactant in the solution becomes less and less. Thus the phase transfer rate decreases as the concentration of surfactant decreases.

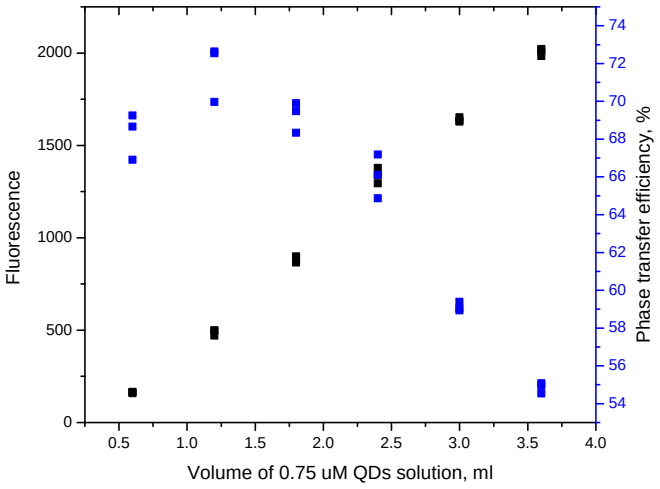


Figure 3.23: Fluorescence and phase transfer efficiency vs. QDs solution volume, 0.75 μM QDs, 900 rpm, 20 ml 1000 ppm sodium decanoate solution

3.8.7 Stability of phase transferred QDs

The stability information was first obtained through fluorescence reading as in figure 3.24. Water phase fluorescence continues to decrease in the figure and the half-life is about two days. The fluorescence loss could be caused by structure damage on the surface of the QDs. So further confirmation is needed to see whether there is really precipitation. After two weeks, samples were taken from the solution. In figure 3.25, "A" was the sample taken from the surface of the solution, without any disturbing to the solution after two weeks of settlement. "C" was the sample taken from the bottom of the solution after two weeks of settlement. After fierce shaking, sample was taken as "B". The samples from solution surface has the lowest fluorescence, and the bottom has the highest. After shaking, the fluorescence is in between. This phenomenon proves the QDs concentration difference within the different levels of the solution. And the difference can be buffered by shaking. So it seems like it is the precipitation.

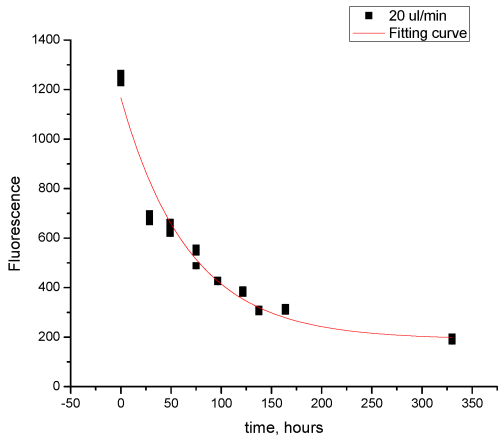


Figure 3.24: Fluorescence of phase-transferred quantum dot solution over two weeks

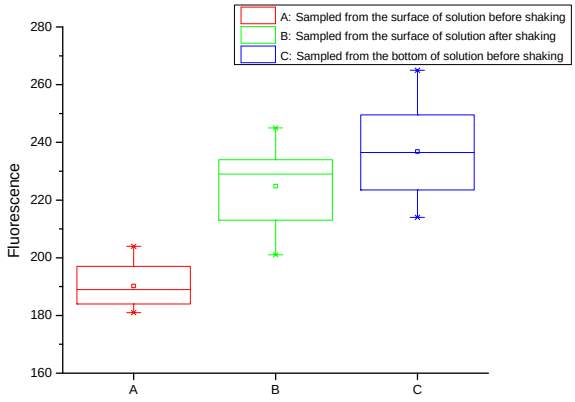


Figure 3.25: Separate the solution from the vial

To confirm the aggregates of the phase transferred QDs in water phase, dynamic light scattering was used. The black plot in figure 3.26 is the size distribution right after the phase transfer. Most of the volume of the QDs is at the diameter around 400 nm. After four days, in the solution, the aggregates around 200 nm remained. And diameter greater than 300 nm disappeared in the solution. However, after shaking, a large portion of the volume shifted to the diameter of several micrometer. That was the settlements. So this figure confirmed the aggregation of phase transferred QDs of relatively large size.

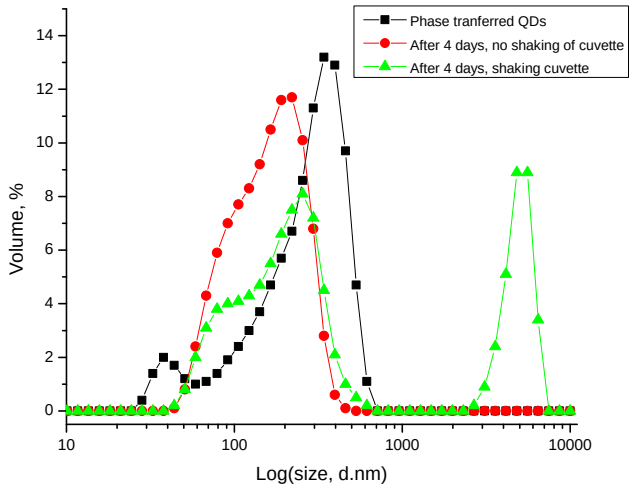
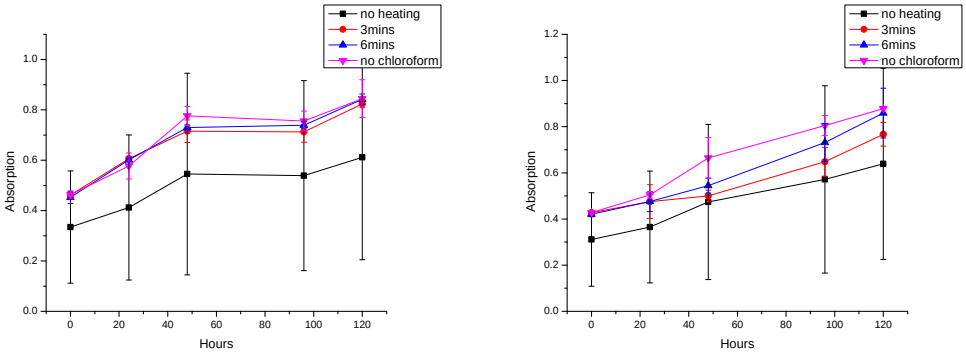


Figure 3.26: Size distribution by volume, 0.6 ml 0.75 μM QDs, 900 rpm, 20 ml 1000 ppm sodium decanoate solution

Actually, the eternal aggregates size is always decided by the strength of the surfactant. The hydrophilic end of the surfactant decides the stability of the QDs. Because sodium decanoate is not a great surfactant, it is expectable for the phase transferred QDs with sodium decanoate to aggregate.

3.9 Toxicity of phase-transferred quantum dots in *Synechococcus elongatus*

First, the toxicity of chloroform had to be excluded. 6 ml chloroform was injected into 20 ml 1000 mg/L sodium decanoate solution at the flow rate of 50 ul/min. Stirring was applied during injection at 900 rpm. After the solution was cooled down, 3 ml cyanobacteria culture was injected with 30 ul product solution. Figure 3.27a showed the effect of heating time after the phase transfer reaction. Absorption indicated the concentration of living cyanobacteria. As figure 3.27a shows, the one without any heating significantly killed the cyanobacteria. And 3 minutes and 6 minutes heating were similar to no chloroform.



(a) 3 ml cyanobacteria with 30 ul solution (b) 3 ml cyanobacteria with 100 ul solution

Figure 3.27: Evaporation of chloroform residue and toxicity of phase transferred QDs

When the volume of production solution was increased to 100 ul, the result was shown in figure 3.27b. As it showed, 6 minutes heating had the same absorption as the null one. And the 3 min group was slightly lower. So for a 100 ul QDs solution test, 6 minutes heating was needed.

Inject 6 ml 0.75 μM QDs solution into 20 ml 1000 mg/L sodium decanoate solution at flow rate of 50 ul/min. It was stirred at 900 rpm. After the phase transfer, it was heated at 550 °C degree hotplate temperature for 6 minutes. And the product solution was cooled down and added into 3

ml cyanobacteria culture.

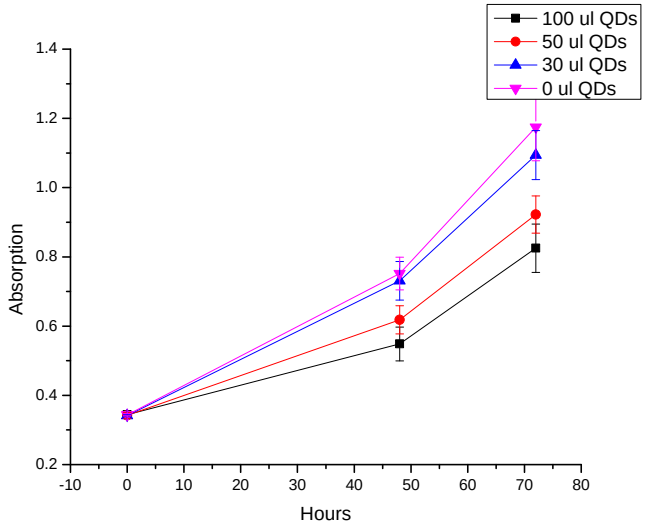


Figure 3.28: 3 ml cyanobacteria absorption curve with different volumes of QDs water solution

Figure 3.28 showed the relationship between the product added in the culture and the culture absorption. As it shows, the number of living cyanobacteria decreased as the amount of QDs solution increased. It proved the toxicity of this phase transferred QDs.

Chapter 4

Conclusions

1. Five scenarios have been studied. If the water insoluble QDs are dried first, and then contact natural water, the environmental impact would be very small. In the scenario where organic solvent relatively stably exists in the natural water, flocculates of QDs aggregates will form at their interface between the two phases and that has little environmental influence either. In the case that QDs in organic solvent spread across the water and slowly dissolves into water, QDs are likely to be phase transferred into the water body and form hydrophilic nanoparticles.

2. In the third scenario, the phase transfer of QDs is highly efficient. When QDs solution is released into natural water, it spreads and solvents slowly dissolves or evaporates, which is just the same as adding QDs solution very slowly. So the phase transfer rate is expected to be high.

3. Locations like wetland are more prone to the damage of QDs release than normal water bodies. Because in the wetland, the natural surfactant concentration is higher than normal.

4. The stability of the phase transferred QDs is decided by the wettability of the hydrophilic end of the surfactant and the size of the aggregates. The stronger the surfactant, and the smaller the phase transferred QDs, the more likely for the QDs to actively stay in the environment

5. The phase transferred QDs shows toxicity on cyanobacteria.

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